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(54) Title: OXIDATION OF 5-(HYDROXYMETHYL) FURFURAL TO 2,5-DIFORMYLFURAN AND SUBSEQUENT DECARBONYLATION TO UNSUBSTITUTED FURAN

(57) Abstract: Alcohols are catalytically oxidized to aldehydes, in particular to benzaldehyde and diformylfuran, which are useful as intermediates for a multiplicity of purposes. The invention also relates to the polymerization of the dialdehyde and to the decarbonylation of the dialdehyde to furan.

TITLE

OXIDATION OF 5-(HYDROXYMETHYL) FURFURAL TO
2,5-DIFORMYLFURAN AND SUBSEQUENT DECARBONYLATION
TO UNSUBSTITUTED FURAN

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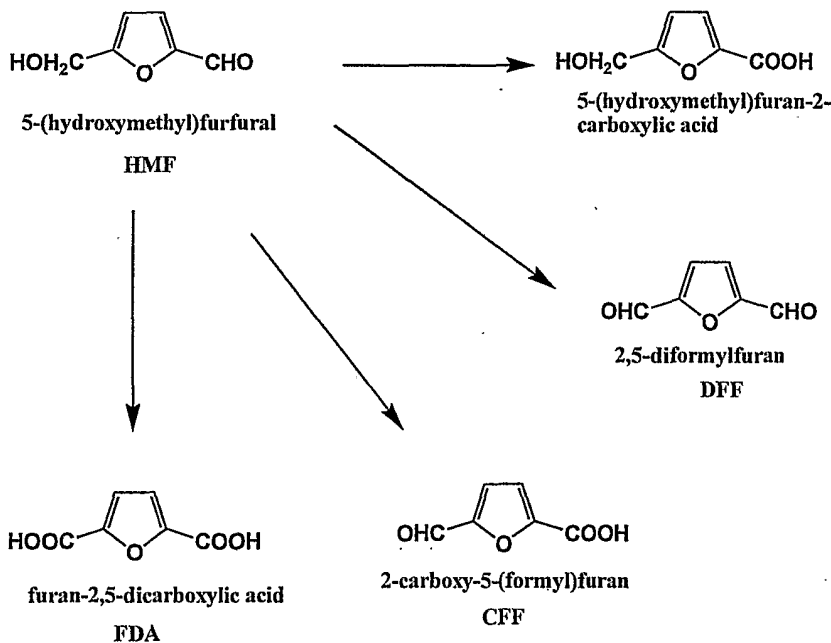
FIELD OF INVENTION

The invention relates to the catalytic oxidation of alcohols to aldehydes, in particular the formation of benzaldehyde and diformylfuran, which are useful as intermediates for a multiplicity of purposes. The invention also relates to the polymerization and the decarbonylation of a dialdehyde.

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BACKGROUND

5-(Hydroxymethyl)furfural (HMF) is a versatile intermediate that can be obtained in high yield from biomass sources such as naturally occurring carbohydrates, including fructose, glucose, sucrose, and starch. Specifically, HMF is a conversion product of hexoses with 6 carbon atoms. It is known that HMF can be oxidized using a variety of reagents to form any of four different products, which can themselves be converted to one or more of the others:



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The selective oxidation of an alcohol functionality in the presence of an aldehyde functionality on the same compound is difficult because of the high reactivity of the aldehyde group. Furthermore, if HMF is reacted with molecular oxygen (O₂), the aldehyde functionality would be expected to oxidize more rapidly than the alcohol and the expected product would be predominantly

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5-(hydroxymethyl)furan-2-carboxylic acid (Sheldon, R. A. and Kochi, J. K.

"Metal Catalyzed Oxidations of Organic Compounds", Academic Press, New York, NY 1981, p 19).

Diformylfuran (DFF) has been prepared from HMF using CrO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ (L. Cottier et al., *Org. Prep. Proced. Int.* (1995), 27(5), 564; JP 54009260) but these methods are expensive and results in large amounts of inorganic salts as waste. Heterogeneous catalysis using vanadium compounds has also been used, but the catalysts have shown low turnover numbers (DE 19615878, Moreau, C. et al., *Stud. Surf. Sci. Catal.* (1997), 108, 399-406). Catalytic oxidation has been demonstrated using hydrogen peroxide (M. P. J. Van Deurzen, *Carbohydrate Chem.* (1997), 16(3), 299) and dinitrogen tetroxide (JP 55049368) which are expensive. The relatively inexpensive molecular oxygen (O_2) has been used with a Pt/C catalyst (U.S. Patent No. 4,977,283) to form both DFF and furan-2,5-dicarboxylic acid (FDA), but yielded low amounts of DFF. Good yields were found for FDA, but only as the disodium salt which resulted in wasteful salt formation during conversion to the acid form.

Metal bromide catalysts have been used to oxidize substituted alkylbenzenes to various products including the oxidation of alkyl to aldehydes, alkyl to alcohols, alkyl to acids, alcohol to acid, and aldehydes to acids (W. Partenheimer, *Catalysis Today*, 23(2), 69-158, (1995)). However, in such cases, the aldehyde product is either a minor component or is quickly oxidized further. FDA has also been prepared using a Co/Mn/Br catalyst from 5-methylfurfural with DFF seen as a minor byproduct (V. A. Slavinskaya, et al., *React. Kinet. Catal. Lett.* (1979), 11(3), 215-20).

DFF has been polymerized to form polypinacols and polyvinyls (Cooke, et al., *Macromolecules* 1991, 24, 1404). However, preparation of polyesters prepared from diformylfuran is not known in the literature.

DFF can also be used to produce unsubstituted furan. Unsubstituted furan is an important commodity in the chemical industry used in the production of tetrahydrofuran. Supported metal catalysts have been used in the decarbonylation of the monoaldehyde furfural to furan, but a basic promoter is required, adding expense and complexity to the process (U.S. Patent No. 3,007,941, U.S. Patent No. 4,780,552).

Considering the aforementioned discussion, there is a need for an inexpensive, high yield process for the preparation of both DFF and FDA that does not produce large amounts of waste products and which lends itself to easy separation and purification. Additionally, there is a need for a high yielding process to prepare unsubstituted furan from relatively inexpensive, renewable sources.

SUMMARY OF THE INVENTION

The invention is directed to a first process for the preparation of a dialdehyde comprising a) contacting a compound containing an alcohol functionality and an aldehyde functionality with an oxidant in the presence of a metal bromide catalyst; and b) optionally isolating the dialdehyde product. A preferred metal bromide catalyst comprises a source of bromine and at least one metal selected from the group consisting of Co and Mn, and optionally containing Zr. More preferably the metal bromide catalyst contains Co.

Preferably the dialdehyde is of the formula $H(C=O)-R-(C=O)H$ and the compound is of the formula $HOH_2C-R-(C=O)H$, wherein R is selected from the group consisting of an optionally substituted C_1-C_{20} alkyl or aryl group. The R groups can be linear or cyclic, or a heterocyclic group. More preferably, R is furan, and most preferably the dialdehyde is 2,5-di(formyl)furan. The process of the present invention can be run in a solvent mixture comprising at least one aliphatic C_2-C_6 monocarboxylic acid compound, preferably acetic acid.

The invention is further directed to a second process for the preparation of a diacid of the formula $HOOC-R'-COOH$ from an alcohol/aldehyde of the formula $HOH_2C-R'-(C=O)H$, wherein R' is an optionally substituted furan ring, comprising the steps:

- (a) contacting the alcohol/aldehyde with an oxidant in the presence of a metal bromide catalyst forming an alcohol/acid having the formula $HOH_2C-R'-COOH$, and optionally isolating the alcohol/acid;
- (b) contacting the alcohol/acid with an oxidant in the presence of a metal bromide catalyst forming an acid/aldehyde having the formula $HOOC-R'-(C=O)H$, and optionally isolating the acid/aldehyde;
- (c) contacting the acid/dialdehyde with an oxidant in the presence of a metal bromide catalyst forming the diacid, optionally isolating the diacid.

The invention is further directed to a third process for the preparation of a diacid of the formula $HOOC-R'-COOH$ from an alcohol/aldehyde of the formula $HOH_2C-R'-(C=O)H$, wherein R' is an optionally substituted furan ring, comprising the steps:

- (a') contacting the alcohol/aldehyde with an oxidant in the presence of a metal bromide catalyst forming a dialdehyde having the formula $H(C=O)-R'-(C=O)H$, and optionally isolating the dialdehyde;

- (b') contacting the dialdehyde with an oxidant in the presence of a metal bromide catalyst forming an acid/aldehyde having the formula HOOC-R'-(C=O)H , and optionally isolating the acid/aldehyde; and
- 5 (c') contacting the acid/dialdehyde with an oxidant in the presence of a metal bromide catalyst forming the diacid, and optionally isolating the diacid.

The process further comprises the steps of a', b', and c' and wherein before step c' the acid/aldehyde is converted to an acetate ester of the formula

10 $\text{CH}_3(\text{C=O})\text{OCH}_2\text{-R'-(C=O)H}$.

Preferably, in the above process the diacid is furan-2,5-dicarboxylic acid and the alcohol/aldehyde is 5-(hydroxymethyl)furfural.

The process can optionally be run in a solvent or solvent mixture comprising at least one aliphatic $\text{C}_2\text{-C}_6$ monocarboxylic acid compound,

15 preferably acetic acid.

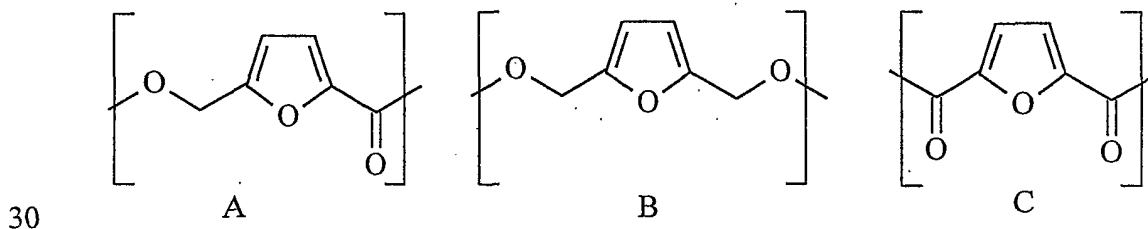
The invention is also directed to a fourth process for the preparation of an aldehyde comprising a) contacting a compound of the formula $\text{AR-CH}_2\text{-OH}$ wherein AR is an optionally substituted aryl with an oxidant in the presence of a metal bromide catalyst; and b) optionally isolating the aldehyde product.

20 Preferably, AR an optionally substituted phenyl group. Most preferably, AR is an unsubstituted phenyl group. A preferred metal bromide catalyst is comprised of a source of bromine and at least one metal selected from the group consisting of Co and Mn. More preferably the metal bromide catalyst contains Co.

The process can be run in a solvent or solvent mixture comprising at least

25 one aliphatic $\text{C}_2\text{-C}_6$ monocarboxylic acid compound, preferably acetic acid.

The invention is also directed to a fifth process to form a polyester polymer and the polyester polymer so produced from 2,5-diformylfuran comprising the repeat units A and B and C.



wherein said process comprises polymerization of di(formyl)furan. The process can be performed in the presence of a catalyst of the formula $\text{M}^{+n}(\text{O-Q})_n$ wherein M is a metal, n is the positive charge on the metal, and Q is an alkyl

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